

# THE MAXIMAL EXCESS CHARGE FOR A FAMILY OF DENSITY-MATRIX-FUNCTIONAL THEORIES INCLUDING HARTREE-FOCK AND MÜLLER THEORIES

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ABSTRACT. We will give a proof that the maximal excess charge for an atom described by a family of density-matrix-functionals, which includes Hartree-Fock and Müller theories, is bounded by an universal constant. We will use the new technique introduced by Frank et al [4].

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## 1. INTRODUCTION

A proof of the experimental fact that atoms can at most bind one extra electron is a major challenge in mathematical physics. Even a proof of the weaker bound  $Z + C$  for the maximal electron number is still an open question in full Schrödinger theory and is known as the *ionization conjecture*.

Since full Schrödinger theory is analytically and numerically very complicated, approximate but simpler theories are often used to study atoms. One of the most accurate but still fairly simple approximate theories is the Thomas-Fermi-Dirac-Weizsäcker theory, for which the ionization conjecture was proved very recently [4]. Extending the method in [4] and using Solovej's bootstrap argument in [15], Frank, Nam and Van Den Bosch were able to provide a proof of the ionization conjecture for the more involved Müller theory [5], which relies - just like the Hartree-Fock

functional - on one-particle density matrices rather than merely on electron densities.

We shall see that this method can be used as well to prove the ionization conjecture for a family of density-matrix theories including Müller and Hartree-Fock theories. For any parameter  $p \in [1/2, 1]$  we consider the *Power functional*

$$\mathcal{E}_Z^p(\gamma) = \text{tr} \left( -\Delta\gamma - \frac{Z}{|x|}\gamma \right) + D[\rho_\gamma] - X(\gamma^p),$$

$$D[\rho_\gamma] = \frac{1}{2} \iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} dx dy, \quad X(\gamma^p) = \frac{1}{2} \iint \frac{|\gamma^p(x,y)|^2}{|x-y|} dx dy,$$

which was introduced by Sharma et al [11]. Note that  $p \in [1/2, 1]$  interpolates between the Müller functional  $\mathcal{E}_Z^M(\gamma) = \mathcal{E}_Z^{1/2}(\gamma)$  and the Hartree-Fock functional  $\mathcal{E}_Z^{\text{HF}}(\gamma) = \mathcal{E}_Z^1(\gamma)$ .

At this point we want to motivate the choice of the exchange term  $X(\gamma^p)$ . By Lieb's variational principle, the ground state energy of the Hartree-Fock functional gives an upper bound for the Schrödinger ground state energy  $E_S(N, Z)$ . In [3] it is conjectured (indeed proven for  $N = 2$ ) that the ground state energy of the Müller functional is a lower bound of  $E_S(N, Z)$ . Numerical results also support this conjecture. Thus, it is no surprise that theories interpolating between these functionals give good numerical results and get more and more popular among theoretical chemists (e.g. [6, 8, 10]). Recall that the ground state energies of both, the Müller functional and the Hartree-Fock functional of a neutral atoms agree with the quantum ground state energy  $E_S(Z, Z)$  to order  $o(Z^{5/3})$  [2, 12]. Thus, the same correct asymptotic behavior holds true for the Power functional.

For any parameter  $p \in [1/2, 1]$  we will consider the minimization problem

$$E^p(N, Z) := \inf \{ \mathcal{E}_Z^p(\gamma) : \gamma \in \mathcal{I}, \text{tr}(\gamma) = N \}. \quad (1)$$

Here,  $\mathcal{I}$  are fermionic one-particle density matrices, i.e.,

$$\mathcal{I} := \{ \gamma \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) : 0 \leq \gamma \leq 1, \Delta\gamma \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \}$$

where  $\mathfrak{S}_1(L^2(\mathbb{R}^3))$  denotes the trace class operators acting on  $L^2(\mathbb{R}^3)$ . The density is given by  $\rho_\gamma(x) = \gamma(x, x)$ , which can be made rigorous using the spectral decomposition of  $\gamma$ .

If not stated differently, from now on,  $p$  will be any number in  $[1/2, 1]$ . All constants will be independent of  $p$ . Our main theorem will be

**Theorem 1** (Ionization bound). *There is a constant  $C > 0$  such that for all  $Z > 0$ , if the minimization problem  $E^p(N, Z)$  in (1) has a minimizer, then  $N \leq Z + C$ .*

The proof of this theorem works in the same manner as in [5] for the Müller functional. Due to the fractional operator power  $\gamma^p$  it is slightly more involved. The additional technical problems arising for  $1/2 < p < 1$  are proven in Section 2. Apart from this, the main strategy is to compare with Thomas-Fermi theory as in the proof for the Hartree-Fock theory [14, 15]. This is captured in

**Theorem 2** (Screened potential estimate). *Let  $N \geq Z \geq 1$  and let  $\gamma_0$  be a minimizer for  $E^p(N, Z)$ . Let  $\rho^{\text{TF}}$  be the Thomas-Fermi minimizer with  $\int \rho^{\text{TF}} = Z$ . For every  $r > 0$ , define the screened potentials by*

$$\Phi_r(x) = \frac{Z}{|x|} - \int_{|y| \leq r} \frac{\rho_0(y)}{|x-y|} dy, \quad \Phi_r^{\text{TF}} = \frac{Z}{|x|} - \int_{|y| \leq r} \frac{\rho^{\text{TF}}(y)}{|x-y|} dy.$$

Then there are universal constants  $C > 0, \epsilon > 0$  such that

$$\left| \Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x) \right| \leq C(|x|^{-4+\epsilon} + 1)$$

for all  $|x| > 0$ .

The significance of the power  $|x|^{-4+\epsilon}$  is that  $\Phi_{|x|}^{\text{TF}} \sim |x|^{-4}$  for small  $|x|$ .

Similar to [15, 4, 5], we have the following asymptotic estimate for the radii of “infinite atoms”.

**Theorem 3** (Radius estimate). *Let  $\gamma_0$  be a minimizer of  $E^p(N, Z)$  for some  $N \geq Z \geq 1$ . For  $\kappa > 0$ , we define the radius  $R(N, Z, \kappa)$  as the largest number such that*

$$\int_{|x| \geq R(N, Z, \kappa)} \rho_{\gamma_0}(x) dx = \kappa.$$

Then there are universal constants  $C > 0, \epsilon > 0$  such that

$$\limsup_{N \geq Z \rightarrow \infty} \left| R(N, Z, \kappa) - B^{\text{TF}} \kappa^{-1/3} \right| \leq C \kappa^{-\frac{1}{3}-\epsilon}$$

for all  $\kappa \geq C$ , where  $B^{\text{TF}} = 5c^{\text{TF}} \left( \frac{4}{3\pi^2} \right)^{1/3}$ .

Theorem 1 and Theorem 3 will be direct consequences of Theorem 2. To prove Theorem 2 we use Solovej’s bootstrap argument. As in [5], the “multiplying by  $|x|$ ” strategy is not working. This strategy will be replaced - as in [4] and [5] - by a method in which  $\mathbb{R}^3$  will be split into half-planes followed by an averaging process, cf. Section 3.

Having non-existence of a minimizer for  $N \geq Z + C$ , the natural question of existence for a minimizer for  $N \leq Z$  arises. So far, this is open. In [7] it was shown that for any  $N > 0$  and  $Z > 1/2$ , the renormalized Power functional

$$\hat{\mathcal{E}}_Z^p(\gamma) := \mathcal{E}_Z^p(\gamma) - E^p(\text{tr}(\gamma), 0)$$

possesses a minimizer varying over  $\text{tr}(\gamma) \leq N$ . The same method as in [3] was used. However, a proof for the existence of a minimizer for  $E^p(N, Z)$  for  $N \leq Z$  was not given.

*Convention.* Throughout the paper we will assume that  $E^p(N, Z)$  has a minimizer  $\gamma_0$  for some  $N \geq Z$ . The corresponding density will be denoted by  $\rho_0 = \rho_{\gamma_0}$ . Note that in contrast to a minimizer of the Müller functional ( $p = 1/2$ ),  $\rho_0$  need not to be spherically symmetric since the convexity of the functional is lost for  $p > 1/2$ .

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## 2. THE POWER FUNCTIONAL

We will start by proving properties of the Power functional.

**2.1. General facts.** First, we like to note that the ground state energy  $E^p(N, Z)$  is non-decreasing in  $p$ . This can be seen by writing the exchange correlation term as

$$X(\gamma^p) = \frac{1}{2} \int_{\Lambda} \text{tr}(\gamma^p B_{\lambda} \gamma^p B_{\lambda}^*) d\lambda, \quad (2)$$

where  $\Lambda$  is a parameter space. This formula can be derived using Fefferman-de la Llave formula [3, page 4]. Comparing  $E^p(N, Z)$  with the Hartree-Fock energy

$$0 \geq E^{\text{HF}}(N, Z) = E^1(N, Z) \geq E^p(N, Z)$$

already shows that  $E^p(N, Z) \leq 0$  for any  $p \in [1/2, 1]$ ,  $N > 0$ ,  $Z \geq 0$ . Indeed, using subadditivity of the ground state energy for free electrons and a scaled hydrogen minimizer, it can be shown that  $E^p(N, 0) < 0$  for any  $1/2 \leq p < 1$  [7], whereas  $E^{\text{HF}}(N, 0) = 0$ . This means that free electrons have negative (binding) energy for  $1/2 \leq p < 1$ .

Now, we want to prove that  $E^p(N, Z)$  is non-increasing in  $N$ . To this end, we first show that  $E^p(N, Z)$  can be computed varying only over fermionic density matrices with compactly supported integral kernel.

**Lemma 1.** *Let  $Z \geq 0$ ,  $N > 0$  and  $\gamma \in \mathcal{I}$  with  $\text{tr}(\gamma) = N$ . Then, for any  $\epsilon > 0$  there exists a  $\hat{\gamma} \in \mathcal{I}$  with a compactly supported integral kernel,  $\text{tr}(\hat{\gamma}) = N$  and*

$$|\mathcal{E}_Z^p(\gamma) - \mathcal{E}_Z^p(\hat{\gamma})| \leq \epsilon.$$

*Proof.* Let  $\gamma \in \mathcal{I}$  with  $\text{tr}(\gamma) = N$  be given. For  $R > 0$  define  $\gamma_R := \chi_R \gamma \chi_R$ , where  $\chi_R(x) = \chi\left(\frac{|x|}{R}\right)$  and  $\chi : [0, \infty) \rightarrow [0, 1]$  fulfills the following properties:

- $\chi$  is non-increasing and smooth
- $\chi(x) = 1$  for  $x \leq 1$
- $\chi(x) = 0$  for  $x \geq 2$

Hence,  $0 \leq \gamma_R \leq \gamma \leq 1$  and  $\text{tr}(\gamma_R) \leq \text{tr}(\gamma)$ . To guarantee the correct normalization, we define

$$\hat{\gamma}_R(x, y) = \gamma_R(x, y) + c_R \chi_R(x - v) \chi_R(y - v) =: \gamma_R(x, y) + \delta_R(x, y),$$

where  $v \in \mathbb{R}^3$  is arbitrary, but fixed with  $|v| > 5R$ . Also define  $c_R$  by

$$c_R := \frac{\text{tr}(\gamma) - \text{tr}(\gamma_R)}{\int \chi_R(x)^2 dx}. \quad (3)$$

By construction, we have  $\text{tr} \hat{\gamma}_R = \text{tr} \gamma$  and  $0 \leq \gamma_R \leq 1$  for sufficiently large  $R > 0$ .

First, we prove that  $\gamma_R \rightarrow \gamma$  in the space of trace class operators  $\mathfrak{S}_1$ . It suffices to show that for  $R \rightarrow \infty$ ,  $\|\gamma_R\|_{\mathfrak{S}_1} \rightarrow \|\gamma\|_{\mathfrak{S}_1}$  and  $\gamma_R \rightarrow \gamma$  in the weak operator topology. [1, page 47].

Convergence in the weak operator topology follows by Lebesgue's theorem, the pointwise convergence  $\lim_{R \rightarrow \infty} \chi_R(x) \rightarrow 1$  and the fact that

$$\iint |\gamma(x, y) \psi(x) \phi(y)| dx dy \leq \|\gamma\|_{HS} \|\psi\|_{L^2} \|\phi\|_{L^2} \leq \sqrt{\text{tr} \gamma} \|\psi\|_{L^2} \|\phi\|_{L^2}$$

for any  $\phi, \psi \in L^2(\mathbb{R}^3)$ .

Convergence of norms also follows directly using Lebesgue's theorem and the convergence in weak operator sense.

$$\begin{aligned} \lim_{R \rightarrow \infty} \|\gamma_R\|_{\mathfrak{S}_1} &= \lim_{R \rightarrow \infty} \text{tr} \gamma_R = \lim_{R \rightarrow \infty} \sum_{i \in \mathbb{N}} \langle \phi_i, \gamma_R \phi_i \rangle \\ &= \sum_{i \in \mathbb{N}} \lim_{R \rightarrow \infty} \langle \phi_i, \gamma_R \phi_i \rangle = \sum_{i \in \mathbb{N}} \langle \phi_i, \gamma \phi_i \rangle = \text{tr}(\gamma) = \|\gamma\|_{\mathfrak{S}_1}. \end{aligned}$$

Hence,  $\gamma_R \rightarrow \gamma$  in  $\mathfrak{S}_1$  as  $R \rightarrow \infty$ . To show  $\hat{\gamma}_R \rightarrow \gamma$ , it suffices to prove  $\|\delta_R\|_{\mathfrak{S}_1} \xrightarrow{R \rightarrow \infty} 0$ . This holds true, since

$$\|\delta_R\|_{\mathfrak{S}_1} = c_R \int \chi_R(x-v) \chi_R(x-v) dx = c_R \int \chi_R(x)^2 dx = \text{tr} \gamma - \text{tr} \gamma_R$$

and therefore,  $\|\delta_R\|_{\mathfrak{S}_1} \rightarrow 0$ .

Now, we are in the position to prove  $\mathcal{E}_Z^p(\hat{\gamma}_R) \xrightarrow{R \rightarrow \infty} \mathcal{E}_Z^p(\gamma)$ . We start with the kinetic term

$$\text{tr}(-\Delta \hat{\gamma}_R) = \text{tr}(-\Delta \gamma_R - \Delta \delta_R) = \text{tr}(-\Delta \chi_R \gamma \chi_R - \Delta \delta_R).$$

For the first term  $\text{tr}(-\Delta \chi_R \gamma \chi_R) = \|\nabla \chi_R \gamma^{\frac{1}{2}}\|_{HS}^2$ , by Lebesgue's theorem, we have

$$\begin{aligned} \|\nabla \chi_R \gamma^{\frac{1}{2}}\|_{HS}^2 &= \iint |\gamma^{\frac{1}{2}}(x, y) \nabla \chi_R(x) + \chi_R(x) \nabla_x \gamma^{\frac{1}{2}}(x, y)|^2 dx dy \\ &= \iint |\gamma^{\frac{1}{2}}(x, y) R^{-1} \nabla \chi(x) + \chi_R(x) \nabla_x \gamma^{\frac{1}{2}}(x, y)|^2 dx dy \\ &\xrightarrow{R \rightarrow \infty} \iint |\nabla_x \gamma^{\frac{1}{2}}(x, y)|^2 dx dy = \text{tr}(-\Delta \gamma). \end{aligned}$$

The second term can be computed as follows

$$\text{tr}(-\Delta \delta_R) = c_R \int \chi_R(x-v) - \Delta \chi_R(x-v) dx = c_R R \int |\nabla \chi|^2(x) dx \xrightarrow{R \rightarrow \infty} 0,$$

where we used that  $c_R = \mathcal{O}(R^{-3})$ .

Using analogous arguments the convergence of the Coulomb term and the Hartree energy is straightforward to check. We will omit this here and finish by proving the convergence of the exchange term. We will use Hardy's inequality  $-\Delta_x \geq \frac{1}{4}|x-y|^{-2}$  to get

$$\begin{aligned} |X(\gamma^p) - X(\hat{\gamma}_R^p)| &\leq \iint \left| \frac{|\gamma^p(x, y)|^2 - |\hat{\gamma}_R^p(x, y)|^2}{2|x-y|} \right| dx dy \\ &\leq \iint \frac{|\gamma^p(x, y) - \hat{\gamma}_R^p(x, y)| (|\gamma^p(x, y)| + |\hat{\gamma}_R^p(x, y)|)}{2|x-y|} dx dy \\ &\leq \left( \iint |\gamma^p(x, y) - \hat{\gamma}_R^p(x, y)|^2 dx dy \iint \frac{|\gamma^p(x, y)|^2 + |\hat{\gamma}_R^p(x, y)|^2}{4|x-y|^2} dx dy \right)^{1/2} \\ &= \|\gamma^p - \hat{\gamma}_R^p\|_{\mathfrak{S}_2} \left( \iint |\nabla_x \gamma^p(x, y)|^2 + |\nabla_x \hat{\gamma}_R^p(x, y)|^2 dx dy \right)^{1/2} \\ &= \|\gamma^p - \hat{\gamma}_R^p\|_{\mathfrak{S}_2} \left( \text{tr}(-\Delta \gamma^{2p}) + \text{tr}(-\Delta \hat{\gamma}_R^{2p}) \right)^{1/2} \\ &\leq \|\gamma^p - \hat{\gamma}_R^p\|_{\mathfrak{S}_2} (\text{tr}(-\Delta \gamma) + \text{tr}(-\Delta \hat{\gamma}_R))^{1/2}. \end{aligned} \tag{4}$$

Since  $\text{tr}(-\Delta \hat{\gamma}_R) \xrightarrow{R \rightarrow \infty} \text{tr}(-\Delta \gamma)$ , it suffices to show that  $\hat{\gamma}_R^p \rightarrow \gamma^p$  in the Hilbert-Schmidt norm. We have shown that  $\hat{\gamma}_R \rightarrow \gamma$  in  $\mathfrak{S}_1$  and by the continuity of the embedding  $\mathfrak{S}_1 \hookrightarrow \mathfrak{S}_{2p}$ , we deduce that  $\hat{\gamma}_R \rightarrow \gamma$  in  $\mathfrak{S}_{2p}$ . Moreover, the map  $A \mapsto A^p, \mathfrak{S}_{2p} \rightarrow \mathfrak{S}_{2p}$  is continuous for  $A \geq 0$  [13, page 28]. This implies  $\hat{\gamma}_R^p \rightarrow \gamma^p$  in the Hilbert-Schmidt norm and concludes the proof.  $\square$

**Lemma 2** ( $N \mapsto E^p(N, Z)$  is non-increasing). *Given  $N > 0, Z \geq 0$  and any  $M > 0$ . Then,*

$$E^p(N + M, Z) \leq E^p(N, Z) + E^p(M, 0) \leq E^p(N, Z). \quad (5)$$

*Note that  $N \mapsto E^p(N, Z)$  is decreasing for  $1/2 \leq p < 1$  since  $E^p(M, 0) < 0$  in these cases.*

*Proof.* It suffices to prove the first inequality. For a contradiction assume that there exists a  $\delta > 0$  such that

$$E^p(N + M, Z) > E^p(N, Z) + E^p(M, 0) + \delta \quad (6)$$

for some  $N > 0, Z \geq 0$  and  $M > 0$ . Then, there exists a density matrix  $\gamma_N$  with  $\text{tr}(\gamma_N) = N$  such that  $E^p(N, Z) > \mathcal{E}_Z^p(\gamma_N) - \delta/3$ . By Lemma 1 we can assume that  $\gamma_N(x, y)$  has compact support. Choose also a density matrix  $\gamma_M$  with  $\text{tr}(\gamma_M) = M$  such that  $\mathcal{E}_{Z=0}^p(\gamma_M) < E^p(M, 0) + \delta/3$ . We can again assume without loss of generality that  $\gamma_M(x, y)$  is compactly supported. Denote by  $R > 0$  the radius of a ball in  $\mathbb{R}^6$  which contains the supports of  $\gamma_N(x, y)$  and  $\gamma_M(x, y)$ .

For an  $\epsilon > 0$ , we define a translated operator by

$$\tilde{\gamma}_M(x, y) := \gamma_M(x - c, y - c)$$

for a fixed  $c \in \mathbb{R}^3$  satisfying  $|c| > 2R + \frac{1}{\epsilon}$ . Moreover, we define a trial density operator  $\gamma_{N+M}$  to be  $\gamma_{N+M} := \gamma_N + \tilde{\gamma}_M$ . By construction, we have

$$\gamma_N \tilde{\gamma}_M = \tilde{\gamma}_M \gamma_N = 0, \quad 0 \leq \gamma_{N+M} \leq 1,$$

$$\text{tr}(\gamma_{N+M}) = N + M \text{ and } X(\gamma_{N+M}^p) = X(\gamma_N^p) + X(\tilde{\gamma}_M^p).$$

Furthermore, since  $\gamma_N \leq \gamma_{N+M}$ ,

$$\text{tr} \left( -\frac{Z}{|x|} \gamma_{N+M} \right) \leq \text{tr} \left( -\frac{Z}{|x|} \gamma_N \right).$$

For the Hartree term it is easy to see that

$$\iint \frac{\gamma_N(x, x) \tilde{\gamma}_M(y, y)}{2|x - y|} dx dy \leq \frac{\epsilon}{2} \iint \gamma_N(x, x) \tilde{\gamma}_M(y, y) dx dy = \frac{\epsilon NM}{2}$$

and analogously

$$\iint \frac{\gamma_M(x, x) \tilde{\gamma}_N(y, y)}{2|x - y|} dx dy \leq \frac{\epsilon}{2} \iint \gamma_M(x, x) \tilde{\gamma}_N(y, y) dx dy = \frac{\epsilon NM}{2}.$$

Inserting everything into (6) yields

$$\begin{aligned} & \frac{2\delta}{3} + \mathcal{E}_Z^p(\gamma_N) + E^p(M, 0) < E^p(N + M, Z) \leq \mathcal{E}_Z^p(\gamma_{N+M}) \\ & \leq \text{tr}(-\Delta \gamma_N) + \text{tr}(-\Delta \tilde{\gamma}_M) + \text{tr} \left( -\frac{Z}{|x|} \gamma_N \right) + D[\rho_{\gamma_N}] + D[\rho_{\tilde{\gamma}_M}] + \epsilon NM - X(\gamma_N^p) - X(\tilde{\gamma}_M^p) \\ & = \mathcal{E}_Z^p(\gamma_N) + \mathcal{E}_{Z=0}^p(\gamma_M) + \epsilon NM \\ & \leq \mathcal{E}_Z^p(\gamma_N) + E^p(M, 0) + \epsilon NM + \frac{\delta}{3}, \end{aligned}$$

where we have used the translation invariance of  $\mathcal{E}_{Z=0}^p$ . Choosing  $\epsilon = \delta/(3NM)$  gives a contradiction.  $\square$

This directly implies the following binding inequality for the minimizer.

**Corollary 1** (Binding inequality). *For any smooth partition of unity  $\chi_1^2 + \chi_2^2 = 1$  we have*

$$\mathcal{E}_Z^p(\gamma_0) \leq \mathcal{E}_Z^p(\chi_1 \gamma_0 \chi_1) + \mathcal{E}_{Z=0}^p(\chi_2 \gamma_0 \chi_2).$$

## 2.2. Localizing density matrices.

**Lemma 3.** *Let  $\gamma \in \mathcal{I}$  and  $0 \leq \chi(x) \leq 1$  be a smooth function on  $\mathbb{R}^3$ . Then we have for all  $p \in [1/2, 1]$*

$$X(\chi \gamma^p \chi) \leq X((\chi \gamma \chi)^p) \quad (7)$$

and

$$X(\chi \gamma^p) \leq (\text{tr}(-\Delta \chi \gamma \chi))^{\frac{1}{2}} \left( \int \chi^2 \rho_\gamma \right)^{\frac{1}{2}}. \quad (8)$$

*Proof.* We first prove (8). This is obtained using the Cauchy-Schwarz inequality, the Hardy inequality and the fact that  $\gamma^{2p} \leq \gamma$ .

$$\begin{aligned} X(\chi \gamma^p) &= \frac{1}{2} \iint \frac{|\chi(x) \gamma^p(x, y)|^2}{|x - y|} dx dy \\ &\leq \left( \iint \frac{|\chi(x) \gamma^p(x, y)|^2}{4|x - y|^2} dx dy \right)^{\frac{1}{2}} \left( \iint |\chi(x) \gamma^p(x, y)|^2 dx dy \right)^{\frac{1}{2}} \\ &\leq (\text{tr}(-\Delta \chi \gamma^{2p} \chi))^{\frac{1}{2}} \left( \int \chi^2 \rho_\gamma \right)^{\frac{1}{2}} \leq (\text{tr}(-\Delta \chi \gamma \chi))^{\frac{1}{2}} \left( \int \chi^2 \rho_\gamma \right)^{\frac{1}{2}}. \end{aligned}$$

Now, we prove (7). Using (2) it suffices to prove that

$$\chi \gamma^p \chi \leq (\chi \gamma \chi)^p. \quad (9)$$

For  $p = 1$  the inequality is trivial and for  $p = \frac{1}{2}$  it can be shown as follows:

$$\chi \gamma^{\frac{1}{2}} \chi = (\chi \gamma^{\frac{1}{2}} \chi \gamma^{\frac{1}{2}} \chi)^{\frac{1}{2}} \leq (\chi \gamma \chi)^{\frac{1}{2}}.$$

Now, we are left with the case  $p \in (1/2, 1)$ . Setting  $\eta := \gamma^p$ , we can write inequality (9) as

$$\chi \eta \chi \leq (\chi \eta^{\frac{1}{p}} \chi)^p.$$

Since  $1/2 < p < 1$ , it is enough to show that

$$(\chi \eta \chi)^{1/p} \leq \chi \eta^{1/p} \chi. \quad (10)$$

We note that

$$C^{1/p} = c_p \int_0^\infty C^2 (C + z \mathbb{1})^{-1} z^{\frac{1}{p}-2} dz \quad (11)$$

for any non-negative self-adjoint bounded operator  $C$  and some constant  $c_p > 0$ . Hence, inequality (10) holds true, if

$$c_p \int_0^\infty [(\chi \eta \chi)^2 (\chi \eta \chi + z \mathbb{1})^{-1} - \chi \eta^2 (\eta + z \mathbb{1})^{-1} \chi] z^{\frac{1}{p}-2} dz \leq 0.$$

Thus, it suffices to show that

$$\chi (\chi \eta \chi + z \mathbb{1})^{-1} \chi \leq (\eta + z \mathbb{1})^{-1} \quad (12)$$

for all  $z > 0$ .

Note that for self-adjoint bounded operators  $A, B$  with

$$A \geq B > 0 \text{ we have, that } B^{-1} \geq A^{-1}. \quad (13)$$

To use this fact, we approximate  $\chi$  with an invertible operator  $\chi_\epsilon$ . For any  $0 < \epsilon < 1$ , we define

$$\chi_\epsilon(z) = \max(\epsilon, \chi(z)).$$

Obviously,  $\chi_\epsilon \rightarrow \chi$  in norm as  $\epsilon \rightarrow 0$ . In particular, this implies

$$\chi_\epsilon(\chi_\epsilon \eta \chi_\epsilon + z \mathbb{1})^{-1} \chi_\epsilon \rightarrow \chi(\chi \eta \chi + z \mathbb{1})^{-1} \chi$$

for all  $z > 0$ .

Since  $0 < \chi_\epsilon \leq 1$  and  $z > 0$ , we have

$$\eta + z \mathbb{1} \chi_\epsilon^{-2} \geq \eta + z \mathbb{1}.$$

Using (13) it follows that

$$\chi_\epsilon(\chi_\epsilon \eta \chi_\epsilon + z \mathbb{1})^{-1} \chi_\epsilon \leq (\eta + z \mathbb{1})^{-1}.$$

The limit  $\epsilon \rightarrow 0$  shows (12), which concludes the proof.  $\square$

**Corollary 2.** *Let  $\gamma_0$  be a minimizer of  $E^p(N, Z)$ . Then,*

$$\int \rho_0^{\frac{5}{3}} + \text{tr}(-\Delta \gamma_0) + D[\rho_{\gamma_0}] \leq C(Z^{\frac{7}{3}} + N) \quad (14)$$

and

$$X(\gamma_0^p) \leq C(Z^{\frac{7}{3}} + N)^{\frac{1}{2}} N^{\frac{1}{2}}. \quad (15)$$

*Proof.* From (8) we know that

$$X(\gamma_0^p) \leq \text{tr}(-\Delta \gamma_0)^{\frac{1}{2}} N^{\frac{1}{2}}. \quad (16)$$

Using this, the kinetic Lieb-Thirring inequality and the fact that the ground state energy in Thomas-Fermi theory equals a negative constant times  $Z^{\frac{7}{3}}$ , we estimate

$$\begin{aligned} \mathcal{E}_Z^p(\gamma_0) &\geq \frac{1}{4} \text{tr}(-\Delta \gamma_0) + \tilde{C} \int \rho_0^{\frac{5}{3}} - Z \int \frac{\rho_0(x)}{|x|} + D[\rho_0] - CN \\ &\geq \frac{1}{4} \text{tr}(-\Delta \gamma_0) + \frac{\tilde{C}}{2} \int \rho_0^{\frac{5}{3}} + \frac{1}{2} D[\rho_0] - CZ^{\frac{7}{3}} - CN. \end{aligned}$$

The fact that  $\mathcal{E}_Z^p(\gamma_0) \leq 0$  implies (14). This also shows  $\text{tr}(-\Delta \gamma_0) \leq C(Z^{\frac{7}{3}} + N)$  which proves (15) using (16).  $\square$

**Lemma 4** (IMS-type formula). *For all quadratic partitions of unity  $\sum_{i=1}^n f_i^2 = 1$  with  $\nabla f_i \in L^\infty$  and for all density matrices  $0 \leq \gamma \leq 1$  with  $\text{tr}((1 - \Delta)\gamma) < \infty$ , we have*

$$\begin{aligned} \sum_{i=1}^n \mathcal{E}_Z^p(f_i \gamma f_i) - \mathcal{E}_Z^p(\gamma) &\leq \int \left( \sum_{i=1}^n |\nabla f_i(x)|^2 \right) \rho_\gamma(x) dx \\ &\quad + \sum_{i < j}^n \iint \frac{f_i(x)^2 (|\gamma^p(x, y)|^2 - \rho_\gamma(x) \rho_\gamma(y)) f_j(y)^2}{|x - y|} dx dy. \end{aligned} \quad (17)$$



*Proof.* We estimate the kinetic term using the IMS-formula to obtain

$$\sum_{i=1}^n \operatorname{tr}(-\Delta f_i \gamma f_i) - \operatorname{tr}(-\Delta \gamma) = \operatorname{tr} \left( \left( \sum_{i=1}^n |\nabla f_i|^2 \right) \gamma \right) = \int \left( \sum_{i=1}^n |\nabla f_i|^2 \right) \rho_\gamma.$$

For the direct term we have

$$\sum_{i=1}^n D[\rho_{f_i \gamma f_i}] = \sum_{i=1}^n D[f_i^2 \rho_\gamma] = D[\rho_\gamma] - \sum_{i < j}^n \iint \frac{f_i(x)^2 \rho_\gamma(x) \rho_\gamma(y) f_j(y)^2}{|x - y|} dx dy.$$

The exchange term can be estimated using (7) to get

$$\begin{aligned} - \sum_{i=1}^n X((f_i \gamma f_i)^p) &\leq - \sum_{i=1}^n X(f_i \gamma^p f_i) \\ &= -X(\gamma^p) + \sum_{i < j}^n \iint \frac{f_i^2(x) |\gamma^p(x, y)|^2 f_j^2(y)}{|x - y|} dx dy. \end{aligned}$$

□

The rest of the paper will be completely analogous to the corresponding parts in [5] and [4]. For convenience of the reader it is included here as well.

### 3. EXTERIOR $L^1$ -ESTIMATE

In this section we control  $\int_{|x| > r} \rho_0$ . First, we recall the screened nuclear potential

$$\Phi_r(x) = \frac{Z}{|x|} - \int_{|y| < r} \frac{\rho_0(y)}{|x - y|} dy.$$

We also introduce the cut-off function

$$\chi_r^+ = \mathbb{1}(|x| > r)$$

and a smooth function  $\eta_r : \mathbb{R}^3 \rightarrow [0, 1]$  satisfying

$$\chi_r^+ \geq \eta_r \geq \chi_{(1+\lambda)r}^+, \quad |\nabla \eta_r| \leq C(\lambda r)^{-1} \quad (18)$$

for some  $\lambda > 0$ .

**Lemma 5.** *For all  $r > 0, s > 0, \lambda \in (0, 1/2]$  we have*

$$\begin{aligned} \int \chi_r^+ \rho_0 &\leq C \int_{r \leq |x| < (1+\lambda)^2 r} \rho_0 + C \left( \sup_{|z| > r} [z|\Phi_r(z)]_+ + s + \lambda^{-2} s^{-1} + \lambda^{-1} \right) \\ &\quad + C (s^2 \operatorname{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{3/5} + C (s^2 \operatorname{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/3}. \end{aligned}$$

*Proof.* Recall from Corollary 1 that the minimizer  $\gamma_0$  fulfills the binding inequality

$$\mathcal{E}_Z^p(\gamma) \leq \mathcal{E}_Z^p(\chi_1 \gamma \chi_1) + \mathcal{E}_{Z=0}^p(\chi_2 \gamma \chi_2) \quad (19)$$

for any smooth partition of unity  $\chi_1^2 + \chi_2^2 = 1$ .

For fixed  $\lambda \in (0, 1/2], s > 0, l > 0, \nu \in \mathbb{S}^2$  we choose

$$\chi_1(x) = g_1 \left( \frac{\nu \cdot \theta(x) - l}{s} \right), \quad \chi_2(x) = g_2 \left( \frac{\nu \cdot \theta(x) - l}{s} \right),$$

where  $g_1, g_2 : \mathbb{R} \rightarrow \mathbb{R}$  and  $\theta : \mathbb{R}^3 \rightarrow \mathbb{R}^3$  satisfy

$$\begin{aligned} g_1^2 + g_2^2 &= 1, \quad g_1(t) = 1 \text{ if } t \leq 0, \quad g_1(t) = 0 \text{ if } t \geq 1, \quad |g_1'| + |g_2'| \leq C, \\ |\theta(x)| &\leq |x|, \quad \theta(x) = 0 \text{ if } |x| \leq r, \quad \theta(x) = x \text{ if } |x| \geq (1 + \lambda)r \text{ and } |\nabla \theta| \leq C\lambda^{-1}. \end{aligned}$$

Now, we begin to estimate the binding inequality (19) using the IMS-type formula (17).

$$\begin{aligned} &\mathcal{E}_Z^p(\chi_1 \gamma_0 \chi_1) + \mathcal{E}_Z^p(\chi_2 \gamma_0 \chi_2) - \mathcal{E}_Z^p(\gamma_0) \\ &\leq \int (|\nabla \chi_1|^2 + |\nabla \chi_2|^2) \rho_0 + \int \frac{Z \chi_2^2 \rho_0(x)}{|x|} dx \\ &\quad + \iint \frac{\chi_2^2(x) (|\gamma_0^p(x, y)|^2 - \rho_0(x) \rho_0(y)) \chi_1^2(y)}{|x - y|} dx dy. \end{aligned}$$

By construction we have

$$\int (|\nabla \chi_1|^2 + |\nabla \chi_2|^2) \rho_0 \leq C(1 + (\lambda s)^{-2}) \int_{\nu \cdot \theta(x) - s \leq l \leq \nu \cdot \theta(x)} \rho_0(x) dx.$$

For the attraction and direct terms, we can estimate

$$\begin{aligned} &\int \frac{Z \chi_2^2(x) \rho_0(x)}{|x|} dx - \iint \frac{\chi_2^2(x) \rho_0(x) \chi_1^2(y) \rho_0(y)}{|x - y|} dx dy \\ &= \int \chi_2^2(x) \rho_0(x) \Phi_r(x) dx - \iint_{|y| \geq r} \frac{\chi_2^2(x) \rho_0(x) \chi_1^2(y) \rho_0(y)}{|x - y|} dx dy \\ &\leq \int_{l \leq \nu \cdot \theta(x)} \rho_0(x) [\Phi_r(x)]_+ dx - \iint_{|y| \geq r, \nu \cdot \theta(y) \leq l \leq \nu \cdot \theta(x) - s} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy. \end{aligned}$$

Since  $\theta(x) = x$  when  $|x| \geq (1 + \lambda)r$ , we obtain

$$\iint_{|y| > r, \nu \cdot \theta(y) \leq \nu \cdot \theta(x) - s} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \geq \iint_{\substack{|x|, |y| \geq (1 + \lambda)r \\ \nu \cdot y \leq l \leq \nu \cdot x - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy.$$

For the exchange-correlation term, we use

$$\iint \frac{\chi_2^2(x) |\gamma_0^p(x, y)|^2 \chi_1^2(y)}{|x - y|} dx dy \leq \iint_{\nu \cdot \theta(y) - s \leq l \leq \nu \cdot \theta(x)} \frac{|\gamma_0^p(x, y)|^2}{|x - y|} dx dy. \quad (20)$$

Now we apply these results to the binding inequality (19) to obtain

$$\begin{aligned} &\iint_{\substack{|x|, |y| \geq (1 + \lambda)r \\ \nu \cdot y \leq l \leq \nu \cdot x - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \leq C(1 + (\lambda s)^{-2}) \int_{\nu \cdot \theta(x) - s \leq l \leq \nu \cdot \theta(x)} \rho_0(x) dx \\ &+ \int_{l \leq \nu \cdot \theta(x)} \rho_0(x) [\Phi_r(x)]_+ dx + \iint_{\nu \cdot \theta(y) - s \leq l \leq \nu \cdot \theta(x)} \frac{|\gamma_0^p(x, y)|^2}{|x - y|} dx dy \end{aligned} \quad (21)$$

for all  $s > 0, l > 0$  and  $\nu \in \mathbb{S}^2$ . Now we want to integrate (21) over  $l \in (0, \infty)$  and then average over  $\nu \in \mathbb{S}^2$ . To do so, we first write the left side as follows.

$$\begin{aligned} &\int_{\mathbb{S}^2} \frac{d\nu}{4\pi} \int_0^\infty dl \iint_{\substack{|x|, |y| \geq (1 + \lambda)r \\ \nu \cdot y \leq l \leq \nu \cdot x - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \\ &= \frac{1}{2} \int_{\mathbb{S}^2} \frac{d\nu}{4\pi} \int_0^\infty dl \iint_{\substack{|x|, |y| \geq (1 + \lambda)r \\ \nu \cdot y \leq l \leq \nu \cdot x - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \\ &\quad + \frac{1}{2} \int_{\mathbb{S}^2} \frac{d\nu}{4\pi} \int_0^\infty dl \iint_{\substack{|x|, |y| \geq (1 + \lambda)r \\ -\nu \cdot x \leq l \leq -\nu \cdot y - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \end{aligned}$$

In the second term we used the symmetries  $\nu \mapsto -\nu$  and  $x \leftrightarrow y$ . For  $a := \nu \cdot x$  and  $b := \nu \cdot y$  remark that

$$\int_0^\infty \mathbb{1}(b \leq l \leq a - s) + \mathbb{1}(-a \leq l \leq -b - s) dl \geq [(a - b)_+ - 2s]_+ \geq [a - b]_+ - 2s.$$

Also note that

$$\int_{\mathbb{S}^2} [\nu \cdot z]_+ \frac{d\nu}{4\pi} = \frac{|z|}{4}$$

for any  $z \in \mathbb{R}^3$  and

$$\int_0^\infty \mathbb{1}(b - s \leq l \leq a) dl \leq [a - b]_+ + s.$$

We will also use Fubini's theorem to interchange the integrals. For the right hand side, we use the fact that

$$\{x : \nu \cdot \theta(x) \geq l\} \subset \{x : |x| \geq r\}$$

since  $l > 0$  and  $\theta(x) = 0$  when  $|x| < r$ . Thus, after integrating  $l$  from 0 to  $\infty$  and averaging over  $\nu \in \mathbb{S}^2$ , inequality (21) gives

$$\begin{aligned} & \frac{1}{2} \iint_{|x|, |y| \geq (1+\lambda)r} \frac{|x - y|/4 - 2s}{|x - y|} \rho_0(x) \rho_0(y) dx dy \\ & \leq C(s + \lambda^{-2}s^{-1}) \int_{|x| \geq r} \rho_0(x) dx + \int_{|x| \geq r} [|\theta(x)|/4 \Phi_r(x)]_+ \rho_0(x) dx \\ & \quad + \iint_{|x| \geq r} \frac{|\theta(x) - \theta(y)|/4 + s}{|x - y|} |\gamma_0^p(x, y)|^2 dx dy. \end{aligned}$$

Using  $|\theta(x)| \leq |x|$  and  $|\theta(x) - \theta(y)| \leq C\lambda^{-1}|x - y|$ , this simplifies to

$$\begin{aligned} \frac{1}{8} \left( \int \chi_{(1+\lambda)r}^+ \rho_0 \right)^2 & \leq \left( \frac{1}{4} \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_r^+ \rho_0 \\ & \quad + sD[\chi_{(1+\lambda)r}^+ \rho_0] + s \iint \frac{\chi_r^+(x) |\gamma^p(x, y)|^2}{|x - y|} dx dy. \end{aligned}$$

Now, we replace  $r$  by  $(1 + \lambda)r$  to get

$$\begin{aligned} & \frac{1}{8} \left( \int \chi_{(1+\lambda)^2r}^+ \rho_0 \right)^2 \leq \\ & \left( \frac{1}{4} \sup_{|z| \geq (1+\lambda)r} [|z| \Phi_{(1+\lambda)r}(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_{(1+\lambda)r}^+ \rho_0 \\ & \quad + sD[\chi_{(1+\lambda)^2r}^+ \rho_0] + s \iint \frac{\chi_{(1+\lambda)r}^+(x) |\gamma^p(x, y)|^2}{|x - y|} dx dy. \end{aligned} \tag{22}$$

First, we estimate the left hand side of (22).

$$\left( \int \chi_{(1+\lambda)^2r}^+ \rho_0 \right)^2 \geq \frac{1}{2} \left( \int \chi_r^+ \rho_0 \right)^2 - \left( \int_{r < |x| < (1+\lambda)^2r} \rho_0 \right)^2.$$

Now we also estimate the right side of (22). For the first term we use  $\Phi_{(1+\lambda)r}(z) \leq \Phi_r(z)$  and  $\chi_{(1+\lambda)r} \leq \chi_r$  to get

$$\begin{aligned} & \left( \frac{1}{4} \sup_{|z| \geq (1+\lambda)r} [|z| \Phi_{(1+\lambda)r}(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_{(1+\lambda)r}^+ \rho_0 \\ & \leq \left( \frac{1}{4} \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_r^+ \rho_0. \end{aligned}$$

For the second term we use the Hardy-Littlewood-Sobolev, the Hölder and the Lieb-Thirring inequalities to obtain

$$\begin{aligned} D[\chi_{(1+\lambda)^2r}^+ \rho_0] & \leq C \|\chi_{(1+\lambda)r} \rho_0\|_{L^{6/5}}^2 \leq C \|\chi_{(1+\lambda)r} \rho_0\|_{L^1}^{7/6} \|\chi_{(1+\lambda)r} \rho_0\|_{L^{5/3}}^{5/6} \\ & \leq C \|\chi_r^+ \rho_0\|_{L^1}^{7/6} (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/2}. \end{aligned}$$

We also used  $\eta_r^2 \geq \chi_{(1+\lambda)^2r}^+$ . For the third term we use (8) to get

$$\begin{aligned} & \iint \frac{\chi_{(1+\lambda)r}^+(x) |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \leq \iint \frac{\eta_r(x)^2 |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \\ & \leq 2 (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/2} \left( \int \chi_r^+ \rho_0 \right)^{1/2}. \end{aligned}$$

Putting all the estimates in (22) we end up with

$$\begin{aligned} \left( \int \chi_r^+ \rho_0 \right)^2 & \leq C \left( \int_{r < |x| < (1+\lambda)^2r} \rho_0 \right)^2 \\ & \quad + C \left( \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + s + \lambda^{-2}s^{-1} + \lambda^{-1} \right) \int \chi_r^+ \rho_0 \\ & \quad + Cs \left( \int \chi_r^+ \rho_0 \right)^{\frac{7}{6}} (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{\frac{1}{2}} \\ & \quad + Cs (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{\frac{1}{2}} \left( \int \chi_r^+ \rho_0 \right)^{\frac{1}{2}}. \end{aligned}$$

Hence, by Young's inequality,

$$\begin{aligned} \int \chi_r^+ \rho_0 & \leq C \int_{r < |x| < (1+\lambda)^2r} \rho_0 + C \left( \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + s + \lambda^{-2}s^{-1} + \lambda^{-1} \right) \\ & \quad + C (s^2 \text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{3/5} + C (s^2 \text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/3}. \end{aligned}$$

□

From this proof we already get an upper bound on the excess charge.

**Corollary 3.** *For the minimizer  $\gamma_0$  we have*

$$\text{tr} \gamma_0 = N \leq 2Z + C(Z^{\frac{2}{3}} + 1). \quad (23)$$

Moreover,

$$\int \rho_0^{\frac{5}{3}} + \text{tr}(-\Delta \gamma_0) + D[\rho_0] \leq C(Z^{\frac{7}{3}} + 1) \quad (24)$$

and

$$X(\gamma_0^p) \leq C(Z^{\frac{5}{3}} + 1). \quad (25)$$

*Proof.* Choosing  $\lambda = \frac{1}{2}$  and  $r \rightarrow 0^+$  in (22) leads to

$$N^2 \leq (2Z + Cs + Cs^{-1}C)N + CsD[\rho_0] + CsX(\gamma_0^p).$$

Optimizing over  $s > 0$  we deduce that

$$N \leq 2Z + C + C((D[\rho_0] + X(\gamma_0^p) + N)N^{-1})^{\frac{1}{2}}. \quad (26)$$

Using the bounds from Corollary 2 we get

$$D[\rho_0] + X(\gamma^p) \leq C(Z^{\frac{7}{3}} + N).$$

Inserting this in (26) proves (23). Then, the bounds (24) and (25) follow from Corollary 2.  $\square$

#### 4. SPLITTING OUTSIDE FROM INSIDE

In this section we want to estimate the difference of a reduced Hartree-Fock energy between the minimizer  $\gamma_0$  and other density matrices away from the nucleus. The reduced Hartree-Fock functional is given by

$$\mathcal{E}_r^{\text{RHF}}(\gamma) = \text{tr}(-\Delta\gamma) - \int \Phi_r(x)\rho_\gamma(x)dx + D[\rho_\gamma]. \quad (27)$$

Note that this functional depends on the minimizer  $\gamma_0$ . First, recall that we have introduced a smooth cut-off function  $\eta_r : \mathbb{R}^3 \rightarrow [0, 1]$  satisfying

$$\chi_r^+ \leq \eta_r \leq \chi_{(1+\lambda)r}^+ \quad (28)$$

with  $\lambda \in (0, 1/2]$ . Now we choose a quadratic partition of unity  $\eta_-^2 + \eta_{(0)}^2 + \eta_r^2 = 1$  with

$$\begin{aligned} \text{supp } \eta_- &\subset \{|x| \leq r\}, \quad \text{supp } \eta_{(0)} \subset \{(1-\lambda)r \leq |x| \leq (1+\lambda)r\}, \\ \eta_-(x) &= 1 \text{ if } |x| \leq (1-\lambda)r, \quad |\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2 \leq C(\lambda r)^{-2}. \end{aligned}$$

We will prove

**Lemma 6.** *For all  $r > 0$ , all  $\lambda \in (0, 1/2]$ , all density matrices  $0 \leq \gamma \leq 1$  satisfying  $\text{supp } \rho_\gamma \subset \{x : |x| \geq r\}$  and  $\text{tr } \gamma \leq \int \chi_r^+ \rho_0$  we have*

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{RHF}}(\gamma) + \mathcal{R},$$

where

$$\begin{aligned} \mathcal{R} &\leq C(1 + (\lambda r)^{-2}) \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0 + C\lambda^3 r^3 \sup_{|z| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{5/2} \\ &\quad + C(\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/2} \left( \int \eta_r \rho_0 \right)^{1/2}. \end{aligned}$$

*Proof.* It suffices to show that

$$\mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - \mathcal{R} \leq \mathcal{E}_Z^p(\gamma_0) \leq \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\gamma). \quad (29)$$

**Upper bound.** Since  $\gamma_0$  is a minimizer and by Lemma 2, we have

$$\mathcal{E}_Z^p(\gamma_0) \leq \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_- + \gamma). \quad (30)$$

Since  $\eta_-$  and  $\rho_\gamma$  have disjoint supports, we have

$$(\eta_- \gamma_0 \eta_- + \gamma)^p = (\eta_- \gamma_0 \eta_-)^p + \gamma^p$$

and

$$|(\eta_- \gamma_0 \eta_- + \gamma)^p(x, y)|^2 = |(\eta_- \gamma_0 \eta_-)^p(x, y)|^2 + |\gamma^p(x, y)|^2.$$

Hence,

$$X((\eta_- \gamma_0 \eta_- + \gamma)^p) = X((\eta_- \gamma_0 \eta_-)^p) + X(\gamma^p)$$

and

$$\begin{aligned} \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_- + \gamma) &= \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_Z^p(\gamma) + \iint \frac{\eta_-^2(x) \rho_0(x) \rho_\gamma(y)}{|x - y|} dx dy \\ &\leq \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_{r=0}^{\text{RHF}}(\gamma) + \iint_{|x| \geq r} \frac{\rho_0(x) \rho_\gamma(y)}{|x - y|} \\ &= \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\gamma). \end{aligned}$$

Inserting this in (30) finishes the proof of the upper bound.

**Lower bound.** Using the IMS-type formula (17) and properties of the partition of unity, we have

$$\begin{aligned} \mathcal{E}_Z^p(\gamma_0) &\geq \mathcal{E}_Z^p(\eta_- \gamma_0 \eta_-) + \mathcal{E}_Z^p(\eta_{(0)} \gamma_0 \eta_{(0)}) + \mathcal{E}_Z^p(\eta_r \gamma_0 \eta_r) \\ &\quad - \int (|\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2) \rho_0 \\ &\quad + \iint \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y) (\eta_-(y)^2 + \eta_{(0)}(y)^2)}{|x - y|} dx dy \\ &\quad + \iint \frac{\eta_{(0)}^2(x) \rho_0(x) \rho_0(y) \eta_-(y)^2}{|x - y|} dx dy \\ &\quad - \iint \frac{(\eta_r^2(x) + \eta_{(0)}^2(x)) |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \end{aligned}$$

and

$$- \int (|\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2) \rho_0 \geq -C(\lambda r)^{-2} \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0.$$

Moreover,

$$\begin{aligned} \mathcal{E}_Z^p(\eta_r \gamma_0 \eta_r) &+ \iint \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y) (\eta_-(y)^2 + \eta_{(0)}(y)^2)}{|x - y|} dx dy - \iint \frac{-\eta_r(x)^2 |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \\ &\geq \mathcal{E}^p(\eta_r \gamma_0 \eta_r) + \iint_{|y| \leq r} \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y)}{|x - y|} - \iint \frac{-\eta_r(x)^2 |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \\ &= \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - X((\eta_r \gamma_0 \eta_r)^p) - \iint \frac{\eta_r(x)^2 |\gamma_0^p(x, y)|^2}{|x - y|} dx dy \\ &\geq \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - 3 (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/2} \left( \int \eta_r^2 \rho_0 \right)^2. \end{aligned}$$

We used (8) twice, once with  $\chi = 1$  for  $X((\eta_r \gamma_0 \eta_r)^p)$  and once with  $\chi = \eta_r$  for  $\iint \frac{\eta_r(x)^2 |\gamma_0^p(x, y)|^2}{|x-y|} dx dy$ . Similarly, we get

$$\begin{aligned}
& \mathcal{E}_Z^p(\eta_{(0)} \gamma_0 \eta_{(0)}) + \iint \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y) \eta_{(0)}(y)^2}{|x-y|} - \iint \frac{\eta_{(0)}(x)^2 |\gamma^p(x, y)|^2}{|x-y|} \\
& \geq \mathcal{E}_Z^p(\eta_{(0)} \gamma_0 \eta_{(0)}) + \iint_{|y| \leq (1-\lambda)r} \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y)}{|x-y|} dx dy \\
& \quad - \iint \frac{\eta_{(0)}(x)^2 |\gamma_0^p(x, y)|^2}{|x-y|} dx dy \\
& = \mathcal{E}_{(1-\lambda)r}^{\text{RHF}}(\eta_{(0)} \gamma_0 \eta_{(0)}) - X((\eta_{(0)} \gamma_0 \eta_{(0)})^p) - \iint \frac{\eta_{(0)} |\gamma_0^p(x, y)|^2}{|x-y|} dx dy \\
& \geq \mathcal{E}_{(1-\lambda)r}^{\text{RHF}}(\eta_{(0)} \gamma_0 \eta_{(0)}) - 3 (\text{tr}(-\Delta \eta_{(0)} \gamma_0 \eta_{(0)}))^{1/2} \left( \int \rho_0 \eta_{(0)}^2 \right)^{1/2} \\
& \geq \text{tr} \left( \left( -\frac{1}{2} \Delta - \Phi_{(1-\lambda)r} \right) \eta_{(0)} \gamma_0 \eta_{(0)} \right) - C \int \eta_{(0)}^2 \rho_0. \tag{31}
\end{aligned}$$

Again, we have used (8). Now, we apply the Lieb-Thirring inequality with  $V = \Phi_{(1-\lambda)r} \mathbb{1}_{\text{supp } \eta_{(0)}}$  to obtain

$$\begin{aligned}
\text{tr} \left( \left( -\frac{1}{2} \Delta - \Phi_{(1-\lambda)r} \right) \eta_{(0)} \gamma_0 \eta_{(0)} \right) & \geq \text{tr} \left( \left[ -\frac{1}{2} \Delta - V \right]_- \right) \geq -C \int V^{\frac{5}{2}} \\
& \geq -C \lambda r^3 \sup_{|x| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2}.
\end{aligned}$$

Plugging this estimate into (31) yields

$$\begin{aligned}
& \mathcal{E}_Z^p(\eta_{(0)} \gamma_0 \eta_{(0)}) + \iint \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y) \eta_{(0)}(y)^2}{|x-y|} - \iint \frac{\eta_{(0)}(x)^2 |\gamma^p(x, y)|^2}{|x-y|} \\
& \geq -C \lambda r^3 \sup_{|x| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2} - C \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0.
\end{aligned}$$

In total we get

$$\begin{aligned}
\mathcal{E}_Z^p(\gamma_0) & \geq \mathcal{E}^p(\eta_- \gamma_0 \eta_0) + \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - C(1 + (\lambda r)^{-2}) \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0 \\
& \quad - C \lambda r^3 \sup_{|x| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2} - 3 (\text{tr}(-\Delta \eta_r \gamma_0 \eta_r))^{1/2} \left( \int \eta_r \rho_0 \right)^{1/2},
\end{aligned}$$

which gives the lower bound in (29).  $\square$

The previous lemma also implies

**Lemma 7.** *For all  $r > 0$  and all  $\lambda \in (0, 1/2]$  we have*

$$\begin{aligned}
\text{tr}(-\Delta \eta_r \gamma_0 \eta_r) & \leq C(1 + (\lambda r)^{-2}) \int \chi_{(1-\lambda)r}^+ \rho_0 + C \lambda r^3 \sup_{|z| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{5/2} \\
& \quad + C \sup_{|z| \geq r} [|z| \Phi_r(z)]_+^{7/3}.
\end{aligned}$$

*Proof.* Applying Lemma 6 to  $\gamma = 0$  gives  $\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{R}$ . Using the Lieb-Thirring inequality and the fact that the ground state energy in Thomas-Fermi theory is a negative constant times  $Z^{7/3}$ , we can bound  $\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r)$  from below:

$$\begin{aligned} \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) &\geq \frac{1}{2} \text{tr}(-\Delta \eta_r \gamma_0 \eta_r) + C^{-1} \int (\eta_r \rho_0)^{5/3} - \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ \int \frac{\eta_r^2 \rho_0}{|x|} + D[\eta_r \rho_0] \\ &= \frac{1}{2} \text{tr}(-\Delta \eta_r \gamma_0 \eta_r) - C \sup_{|z| \geq r} [|z| \Phi_r(z)]_+^{7/3}. \end{aligned}$$

Hence,

$$\text{tr}(-\Delta \eta_r \gamma_0 \eta_r) \leq C\mathcal{R} + C \sup_{|z| \geq r} [|z| \Phi_r(z)]_+^{7/3},$$

which implies the lemma.  $\square$

## 5. A COLLECTION OF USEFUL FACTS

**5.1. Semiclassical analysis.** In order to compare  $\mathcal{E}_Z^p$  with Thomas-Fermi theory, we use a semiclassical approximation. The following results are taken from [15, Lemma 8.2] after optimising over  $\delta > 0$  and replacing  $V$  by  $2V$ . Moreover,  $L_{\text{sc}} = (15\pi^2)^{-1}$ .

**Lemma 8.** *For  $s > 0$ , fix a smooth function  $g : \mathbb{R}^3 \rightarrow [0, 1]$  such that*

$$\text{supp } g \subset \{|x| \leq s\}, \int g^2 = 1, \int |\nabla g|^2 \leq Cs^{-2}. \quad (32)$$

(1) *For all  $V : \mathbb{R}^3 \rightarrow \mathbb{R}$  such that  $[V]_+, [V - V * g^2]_+ \in L^{\frac{5}{2}}$  and for all density matrices  $0 \leq \gamma \leq 1$ , we have*

$$\text{tr}((-\Delta - V)\gamma) \geq -L_{\text{sc}} \int [V]_+^{\frac{5}{2}} - Cs^{-2} \text{tr} \gamma - C \left( \int [V]_+^{\frac{5}{2}} \right)^{\frac{3}{5}} \left( \int [V - V * g^2]_+^{\frac{5}{2}} \right)^{\frac{2}{5}}. \quad (33)$$

(2) *On the other hand, if  $[V]_+ \in L^{\frac{5}{2}} \cap L^{\frac{3}{2}}$ , then there is a density matrix  $\gamma$  such that*

$$\rho_\gamma = \frac{5}{2} L_{\text{sc}} [V]_+^{\frac{3}{2}} * g^2 \quad (34)$$

and

$$\text{tr}(-\Delta \gamma) \leq L_{\text{sc}} \int [V]_+^{\frac{5}{2}} + Cs^{-2} \int [V]_+^{\frac{3}{2}}. \quad (35)$$

**5.2. Coulomb potential estimate.** The following bound is essentially contained in [15, Corollary 9.3] and appears explicitly in [4, Lemma 18].

**Lemma 9.** *For every  $f \in L^{\frac{5}{3}} \cap L^{\frac{6}{5}}$  and  $x \in \mathbb{R}^3$ , we have*

$$\left| \int_{|y| < |x|} \frac{f(y)}{|x - y|} dy \right| \leq C \|f\|_{\frac{5}{3}}^{\frac{5}{6}} (|x| D[f])^{\frac{1}{12}}. \quad (36)$$



## 6. SCREENED POTENTIAL ESTIMATE

**Lemma 10** (Screened potential estimate). *There are universal constants  $C > 0, \epsilon > 0, D > 0$  such that*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon}, \quad \forall |x| \leq D. \quad (37)$$

As in [4], this is proved using a bootstrap argument.

**Lemma 11** (Initial step). *There is a universal constant  $C_1$  such that*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{\frac{49}{36}-a} |x|^{\frac{1}{12}}, \quad \forall |x| > 0 \quad (38)$$

with  $a = 1/198$ .

**Lemma 12** (Iterative step). *There are universal constants  $C_2, \beta, \delta, \epsilon > 0$  such that, if*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \beta|x|^{-4}, \quad \forall |x| \leq D \quad (39)$$

for some  $D \in [Z^{-\frac{1}{3}}, 1]$ , then

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_2|x|^{-4+\epsilon}, \quad \forall D \leq |x| \leq D^{1-\delta}. \quad (40)$$

Now, we want to prove Lemma 10 using Lemma 11 and Lemma 12.

*Proof of Lemma 10.* We set  $\sigma := \max\{C_1, C_2\}$ . Without loss of generality we may assume that  $\beta < \sigma$  and  $\epsilon \leq 3a = \frac{1}{66}$ . We set

$$D_n = Z^{-\frac{1}{3}(1-\delta)^n}, \quad n = 0, 1, 2, \dots$$

From Lemma 11, we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{\frac{49}{36}-a} |x|^{\frac{1}{12}} \leq \sigma|x|^{-4+\epsilon}, \quad \forall |x| \leq D_0 = Z^{-\frac{1}{3}}$$

and some  $\epsilon > 0$  small enough. From Lemma 12, we deduced by induction that for all  $n = 0, 1, 2, \dots$  if

$$\sigma(D_n)^\epsilon \leq \beta,$$

then

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \sigma|x|^{-4+\epsilon}, \quad \forall |x| \leq D_{n+1}.$$

Note that  $D_n \rightarrow 1$  as  $n \rightarrow \infty$  and that  $\sigma > \beta$ . Thus, there is a minimal  $n_0 \in \{0, 1, 2, \dots\}$  such that  $\sigma(D_{n_0})^\epsilon > \beta$ . If  $n_0 \geq 1$ , then  $\sigma(D_{n_0-1})^\epsilon \leq \beta$  and therefore, by the preceding argument,

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \sigma|x|^{-4+\epsilon}, \quad \forall |x| \leq D_{n_0}.$$

As shown above, the same bound holds true for  $n_0 = 0$ . Now, let  $D = (\sigma^{-1}\beta)^{\frac{1}{\epsilon}}$ , which is an universal constant, and note that by choice of  $n_0$  we have  $D_{n_0} \geq D$ .  $\square$

## 7. INITIAL STEP

In this section we prove Lemma 11. We write

$$\mathcal{E}^{\text{RHF}}(\gamma) = \mathcal{E}_{r=0}^{\text{RHF}}(\gamma) = \text{tr}(-\Delta\gamma) - \int \frac{Z\rho_\gamma(x)}{|x|} dx + D[\rho_\gamma].$$

*Proof of Lemma 11.* The strategy is to bound  $\mathcal{E}_Z^p(\gamma_0)$  from above and below using semi-classical estimates from Lemma 8. The main term in both bounds is  $\mathcal{E}^{\text{TF}}(\rho^{\text{TF}})$ , but in the lower bound we will get an additional term  $D[\rho_0 - \rho^{\text{TF}}]$ . The error terms in the upper and lower bounds will then give an upper bound on  $D[\rho_0 - \rho^{\text{TF}}]$  which will imply the lemma.

**Upper bound.** We shall show that

$$\mathcal{E}_Z^p(\gamma_0) \leq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + CZ^{\frac{11}{5}}. \quad (41)$$

Indeed, by Lemma 2,

$$N \mapsto E^p(N, Z)$$

is non-increasing and since the contribution of the exchange term to the energy is non-positive, we have

$$\mathcal{E}_Z^p(\gamma_0) \leq E_{\leq}^p(N, Z) \leq E_{\leq}^{\text{RHF}}(N, Z),$$

where  $E_{\leq}^p(N, Z) = \inf\{\mathcal{E}_Z^p(\gamma) : \gamma \in \mathcal{I}, \text{tr}(\gamma) \leq N\}$  and analogously for  $E_{\leq}^{\text{RHF}}(N, Z)$ . Now, (41) follows from a well-known bound on the ground state energy in reduced Hartree-Fock theory [9, Proof of Theorem 5.1].

**Lower bound.** We now show that

$$\mathcal{E}^p(\gamma_0) \geq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + D[\rho_0 - \rho^{\text{TF}}] - CZ^{\frac{25}{11}}. \quad (42)$$

With the Thomas-Fermi potential  $\varphi^{\text{TF}} = \frac{Z}{|x|} - \rho^{\text{TF}} * |x|^{-1}$  we can write

$$\mathcal{E}^p(\gamma_0) = \text{tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) + D[\rho_0 - \rho^{\text{TF}}] - D[\rho^{\text{TF}}] - X(\gamma_0^p).$$

Recall from (25) the bound

$$X(\gamma_0^p) \leq CZ^{\frac{5}{3}}. \quad (43)$$

Next, from the semiclassical estimate (33) we have

$$\text{tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) \geq -L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{\frac{5}{2}} - Cs^{-2} \text{tr}\gamma_0 - C \left( \int [\varphi^{\text{TF}}]_+^{\frac{5}{2}} \right)^{\frac{3}{5}} \left( [\varphi^{\text{TF}} - \varphi^{\text{TF}} * g^2]_+^{\frac{5}{2}} \right)^{\frac{2}{5}}.$$

According to (23), we can bound  $\text{tr}\gamma_0 = N \leq CZ$ . Moreover, by scaling,

$$\int |\varphi^{\text{TF}}|^{\frac{5}{2}} = C \int (\rho^{\text{TF}})^{\frac{5}{3}} \leq CZ^{\frac{7}{3}}$$

and, as explained in [15, end of page 554],

$$\int |\varphi^{\text{TF}} - \varphi^{\text{TF}} * g^2|^{\frac{5}{2}} \leq CZ^{\frac{5}{2}} s^{\frac{1}{2}}.$$

Thus,

$$\text{tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) \geq -L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{\frac{5}{2}} - CZ^{\frac{25}{11}}.$$

Optimising over  $s > 0$  we get

$$\mathrm{tr}((-\Delta - \varphi^{\mathrm{TF}}(\gamma_0)) \geq -L_{\mathrm{sc}} \int [\varphi^{\mathrm{TF}}]_+^{\frac{5}{2}} - CZ^{\frac{25}{11}}.$$

From the Thomas-Fermi equation we have

$$-L_{\mathrm{sc}} \int [\varphi^{\mathrm{TF}}]_+^{\frac{5}{2}} - D[\rho^{\mathrm{TF}}] = \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}), \quad (44)$$

which proves (42).

**Conclusion.** Combining (41) and (42), we deduce that

$$D[\rho_0 - \rho^{\mathrm{TF}}] \leq CZ^{\frac{25}{11}}.$$

From the Coulomb estimate (9) with  $f = \rho_0 - \rho_0^{\mathrm{TF}}$  and the kinetic estimates

$$\int \rho_0^{\frac{5}{3}} \leq CZ^{\frac{7}{3}}, \quad \int (\rho^{\mathrm{TF}})^{\frac{5}{3}} \leq CZ^{\frac{7}{3}}$$

(the first estimate follows from (14) and the second one from scaling), we find that for all  $|x| > 0$ ,

$$\begin{aligned} |\Phi_{|x|}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)| &= \left| \int_{|y| \leq |x|} \frac{\rho_0(y) - \rho^{\mathrm{TF}}(y)}{|x - y|} dy \right| \\ &\leq C \|\rho_0 - \rho^{\mathrm{TF}}\|^{\frac{5}{6}} (|x| D[\rho_0 - \rho^{\mathrm{TF}}])^{\frac{1}{12}} \\ &\leq CZ^{\frac{179}{132}} |x|^{\frac{1}{12}}. \end{aligned}$$

Since  $179/132 = 49/36 - 1/198$ , this is the desired bound.  $\square$

## 8. ITERATIVE STEP

The goal of this section is to prove Lemma 12. The proof is split into five steps.

**Step 1.** We collect some consequences of (39).

**Lemma 13.** *Assume that (39) holds true for some  $\beta, D \in (0, 1]$ . Then, for all  $r \in (0, D]$ , we have*

$$\left| \int_{|x| < r} (\rho_0 - \rho^{\mathrm{TF}}) \right| \leq \beta r^{-3}, \quad (45)$$

$$\sup_{|x| \geq r} |x| |\Phi_r(x)| \leq Cr^{-3}, \quad (46)$$

$$\int_{|x| > r} \rho_0 \leq Cr^{-3}, \quad (47)$$

$$\int_{|x| > r} \rho_0^{\frac{5}{3}} \leq Cr^{-7}, \quad (48)$$

$$\mathrm{tr}(-\Delta \eta_r \gamma_0 \eta_r) \leq C(r^{-7} + \lambda^{-2} r^{-5}), \quad \forall \lambda \in (0, 1/2]. \quad (49)$$

*Proof.* Let  $r \in (0, D]$ . By Newton's theorem, we have

$$\begin{aligned} \int_{|y| < r} (\rho^{\mathrm{TF}}(y) - \rho_0(y)) dy &= r \int_{\mathbb{S}^2} \left( \int_{|y| < r} \frac{\rho^{\mathrm{TF}}(y) - \rho_0(y)}{|r\nu - y|} dy \right) \frac{d\nu}{4\pi} \\ &= r \int_{\mathbb{S}^2} (\Phi_r(r\nu) - \Phi_r^{\mathrm{TF}}(r\nu)) \frac{d\nu}{4\pi}. \end{aligned}$$

Thus, (45) follows directly from (39).

In order to prove (46) we first use the following bounds from Thomas-Fermi theory:

$$\varphi^{\text{TF}}(x) \leq C|x|^{-4}, \quad \rho^{\text{TF}}(x) \leq C|x|^{-6}.$$

The first bound is proved in Theorem 5.2 of [15]. Note that  $\mu^{\text{TF}} = 0$  since  $\rho^{\text{TF}}$  is the minimizer of a neutral atom. The second estimate can be found in the proof of Lemma 5.3 in [15]. Using these bounds we have for all  $|x| > 0$

$$\Phi_{|x|}^{\text{TF}}(x) = \varphi^{\text{TF}}(x) + \int_{|y|>|x|} \frac{\rho^{\text{TF}}(y)}{|x-y|} dy \leq C|x|^{-4},$$

where Newton's theorem was used to get the bound on the integral. This implies  $\Phi_r^{\text{TF}}(x) \leq Cr^{-4}$  for all  $|x| = r$ . Now, we use the assumptions (39) to obtain

$$\Phi_r(x) = (\Phi_r(x) - \Phi_r^{\text{TF}}(x)) + \Phi_r^{\text{TF}}(x) \leq Cr^{-4} \quad \forall |x| = r.$$

Note that  $\Phi_r(x)$  is harmonic ( $\Delta\Phi_r(x) = 0$ ) for  $|x| > r$  and vanishes at infinity. Thus, we can apply Lemma 19 of [4], which is a consequence of the maximum principle, to obtain

$$\sup_{|x| \geq r} |x|\Phi_r(x) = \sup_{|x|=r} |x|\Phi_r(x) \leq Cr^{-3}.$$

Carrying out the same arguments for  $-\Phi_r(x)$  gives  $-\sup_{|x| \geq r} |x|\Phi_r(x) \leq Cr^{-3}$  which concludes the proof of (46).

Now, we prove (47). Using the assumption (39) and the bound  $\rho^{\text{TF}}(x) \leq C|x|^{-6}$ , we have

$$\begin{aligned} \int_{r/3 < |x| < r} \rho_0 &= \int_{|x| < r} (\rho_0 - \rho^{\text{TF}}) - \int_{|x| < r/3} (\rho_0 - \rho^{\text{TF}}) + \int_{r/3 < |x| < r} \rho^{\text{TF}} \\ &\leq \beta r^{-3} + \beta(r/3)^{-3} + Cr^{-3} \leq Cr^{-3}. \end{aligned} \quad (50)$$

Now, we use Lemma 7 as well as (46) and (50) to get

$$\begin{aligned} \text{tr}(-\Delta\eta_r\gamma_0\eta_r) &\leq C(1 + (\lambda r)^{-2}) \int \chi_{(1-\lambda)r}^+ \rho_0 \\ &\quad + C\lambda r^3 \sup_{|z| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{\frac{5}{2}} + C \sup_{|z| \geq r} [|z|\Phi_r(z)]_+^{\frac{7}{2}} \\ &\leq C \left( (\lambda r)^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2} r^{-5} + r^{-7} \right). \end{aligned} \quad (51)$$

Doing the same estimate again but replacing  $r$  by  $r/3$ , we get

$$\text{tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \leq C \left( (\lambda r)^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2} r^{-5} + r^{-7} \right). \quad (52)$$

From Lemma 5, replacing  $r$  by  $r/3$  and choosing  $s = r$ , we find that

$$\begin{aligned} \int \chi_{r/3}^+ \rho_0 &\leq C \int_{r/3 < |x| < (1+\lambda)^2 r/3} \rho_0 + C \left( \sup_{|z| \geq r/3} [|z|\Phi_{r/3}(z)]_+ + \lambda^{-2} r^{-1} \right) \\ &\quad + C \left( r^2 \text{tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \right)^{\frac{3}{5}} + C \left( r^2 \text{tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \right)^{\frac{1}{3}}. \end{aligned}$$

Inserting (46), (50) and (52) into the latter estimate leads to

$$\begin{aligned} \int \chi_r^+ \rho_0 &\leq \int \chi_{r/3}^+ \rho_0 \leq C(r^{-3} + \lambda^{-2}r^{-1}) + C \left( \lambda^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2}r^{-3} + r^{-5} \right)^{\frac{3}{5}} \\ &\quad + C \left( \lambda^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2}r^{-3} + r^{-5} \right)^{\frac{1}{3}}. \end{aligned}$$

This implies (47) (e.g. choose  $\lambda = 1/2$ ). To obtain (49) we just insert (47) into (51).

We use the kinetic Lieb-Thirring inequality and (49) to obtain

$$\int_{|x|>r} \rho_0^{\frac{5}{3}} \leq \int (\eta_{r/3} \rho_0 \eta_{r/3})^{\frac{5}{3}} \leq C \text{tr}(-\Delta \eta_{r/3} \gamma_0 \eta_{r/3}) \leq C(r^{-7} + \lambda^{-2}r^{-5}).$$

Again, we can choose  $\lambda = 1/2$  to get (48).  $\square$

**Step 2.** Now we introduce the exterior Thomas-Fermi energy functional

$$\mathcal{E}_r^{\text{TF}}(\rho) = c^{\text{TF}} \int \rho^{\frac{5}{3}} - \int V_r \rho + D[\rho], \quad V_r = \chi_r^+ \Phi_r. \quad (53)$$

**Lemma 14.** *The functional  $\mathcal{E}_r^{\text{TF}}(\rho)$  has a unique minimizer  $\rho_r^{\text{TF}}$  over*

$$0 \leq \rho \in L^{\frac{5}{3}}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \quad \int \rho \leq \int \chi_r^+ \rho_0.$$

*The minimizer is supported in  $\{|x| \geq r\}$  and satisfies the Thomas-Fermi equation*

$$\frac{5c^{\text{TF}}}{3} \rho_r^{\text{TF}}(x)^{\frac{2}{3}} = [\varphi_r^{\text{TF}}(x) - \mu_r^{\text{TF}}]_+$$

*with  $\varphi_r^{\text{TF}}(x) = V_r - \rho_r^{\text{TF}} * |x|^{-1}$  and a constant  $\mu_r^{\text{TF}} \geq 0$ . Moreover, if (39) holds true for some  $\beta, D \in (0, 1]$ , then*

$$\int (\rho_r^{\text{TF}})^{\frac{5}{3}} \leq Cr^{-7}, \quad \forall r \in (0, D]. \quad (54)$$

The proof is identical to that of [4, Lemma 21].

**Step 3.** Now we compare  $\rho_r^{\text{TF}}$  with  $\chi_r^+ \rho^{\text{TF}}$ .

**Lemma 15.** *We can choose a universal constant  $\beta > 0$  small enough such that, if (39) holds true for some  $D \in [Z^{-1/3}, 1]$ , then  $\mu_r^{\text{TF}} = 0$  and*

$$\begin{aligned} |\varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x)| &\leq C(r/|x|)^{\zeta} |x|^{-4} \\ |\rho_r^{\text{TF}}(x) - \rho^{\text{TF}}(x)| &\leq C(r/|x|)^{\zeta} |x|^{-6} \end{aligned}$$

*for all  $r \in [Z^{-\frac{1}{3}}, D]$  and for all  $|x| > r$ . Here  $\zeta = (\sqrt{72} - 7)/2 \approx 0.77$ .*

This proof is also identical to that of [4, Lemma 22].

**Step 4.** In this step, we compare  $\rho_r^{\text{TF}}$  with  $\chi_r^+ \rho_0$ .

**Lemma 16.** *Let  $\beta > 0$  be as in Lemma 15. Assume that (39) holds true for some  $D \in [Z^{-\frac{1}{3}}, 1]$ . Then,*

$$D[\chi_r^+ \rho_0 - \rho_r^{\text{TF}}] \leq Cr^{-7+b}, \quad \forall r \in [Z^{-\frac{1}{3}}, D],$$

*where  $b = 1/3$ .*

*Proof.* The strategy is to bound  $\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r)$  from above and from below using the semi-classical estimates from Lemma 8. The main term  $\mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}})$  will cancel, whereas the additional term  $D[\chi_r^+ \rho_0 - \rho_r^{\text{TF}}]$  will be bounded by the error terms, which will give the result.

**Upper bound.** We shall prove that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cr^{-7}(r^{2/3} + \lambda^{-2}r^2 + \lambda). \quad (55)$$

We use Lemma 8 (ii) with  $V_r' = \chi_{r+s}^+ \phi_r^{\text{TF}}$ ,  $s \leq r$  to be chosen later and  $g$  spherically symmetric to obtain a density matrix  $\gamma_r$  as in the statement. Since  $\mu_r^{\text{TF}} = 0$  by Lemma 15, we deduce from the Thomas-Fermi equation in Lemma 14 that

$$\rho_{\gamma_r} = \frac{5}{2} L_{\text{sc}} \left( \chi_{r+s}^+ (\phi_r^{\text{TF}})^{\frac{3}{2}} \right) * g^2 = (\chi_{r+s}^+ \rho_r^{\text{TF}}) * g^2.$$

Note that  $\rho_{\gamma_r}$  is supported in  $\{|x| \geq r\}$  and

$$\text{tr} \gamma_r = \int \rho_{\gamma_r} = \int \chi_{r+s}^+ \rho_r^{\text{TF}} \leq \int \rho_r^{\text{TF}} \leq \int \chi_r \rho_0.$$

Thus, we may apply Lemma 6 and obtain

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{RHF}}(\gamma_r) + \mathcal{R}. \quad (56)$$

By the semiclassical estimate from Lemma 8 (ii)

$$\begin{aligned} \mathcal{E}_r^{\text{RHF}}(\gamma_r) &\leq \frac{3}{2} L_{\text{sc}} \int [V_r']_+^{\frac{5}{2}} + Cs^{-2} \int [V_r']_+^{\frac{3}{2}} - \int \Phi_r (\chi_{r+s}^+ \rho_r^{\text{TF}}) * g^2 + D[\rho_r^{\text{TF}} * g^2] \\ &\leq \frac{3}{2} L_{\text{sc}} \int [V_r']_+^{\frac{5}{2}} - \int \Phi_r \rho_r^{\text{TF}} + D[\rho_r^{\text{TF}}] + Cs^{-2} \int \rho_r^{\text{TF}} \\ &\quad + \int (\Phi_r - \Phi_r * g^2) \chi_{r+s}^+ \rho_r^{\text{TF}} + \int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}} \\ &= \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cs^{-2} \int \rho_r^{\text{TF}} + \int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}}, \end{aligned}$$

where we have used the convexity of  $D$  in the second inequality. The equality in the last line holds true, since  $\Phi_r(x)$  is harmonic when  $|x| > r$  and  $g$  is chosen spherically symmetric.

According to (47) we have

$$\int \rho_r^{\text{TF}} \leq \int \chi_r^+ \rho_0 \leq Cr^{-3}.$$

We now use the fact that  $\rho_r^{\text{TF}} \leq C|x|^{-6}$  for all  $|x| \geq r$ , which follows from Lemma 15. Thus,

$$\int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}} \leq Cr^{-3} \int_{r \leq |x| \leq r+s} |x|^{-1} \rho_r^{\text{TF}} \leq Cr^{-8}s,$$

where we have used (46). Optimising over  $s$  (which leads to  $s \sim r^{5/3}$ ) we obtain

$$\mathcal{E}_r^{\text{RHF}}(\gamma_r) \leq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cr^{-7+2/3}. \quad (57)$$

To estimate  $\mathcal{R}$  we use Lemma 13 and obtain

$$\begin{aligned} \mathcal{R} &\leq C(1 + (\lambda r)^{-2})r^{-3} + C\lambda^3(r^{-4})^{5/2} + C(r^{-7} + \lambda^{-2}r^{-5})^{\frac{1}{2}}(r^{-3})^{\frac{1}{2}} \\ &\leq C(\lambda^{-2}r^{-5} + \lambda r^{-7}). \end{aligned}$$

Combining this with (56) and (57) we get the upper bound (55).

**Lower bound.** We shall prove that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] - Cr^{-7+1/3}. \quad (58)$$

We use Lemma 8 (i) in a way similar to the proof of Lemma 11 to obtain

$$\begin{aligned} \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) &= \text{tr}((-\Delta - \varphi_r^{\text{TF}}) \eta_r \gamma_0 \eta_r) + D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] - D[\rho_r^{\text{TF}}] \\ &\geq -L_{\text{sc}} \int [\varphi_r^{\text{TF}}]_+^{\frac{5}{2}} - Cs^{-2} \int \eta_r^2 \rho_0 \\ &\quad - C \left( \int [\varphi_r^{\text{TF}}]_+^{\frac{5}{2}} \right)^{\frac{3}{5}} \left( \int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{\frac{5}{2}} \right)^{\frac{2}{5}} \\ &\quad + D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] - D[\rho_r^{\text{TF}}] \\ &= \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] - Cs^{-2} \int \eta_r^2 \rho_0 \\ &\quad - C \left( \int [\varphi_r^{\text{TF}}]_+^{\frac{5}{2}} \right)^{\frac{3}{5}} \left( \int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{\frac{5}{2}} \right)^{\frac{2}{5}}. \end{aligned}$$

The last identity was derived using the Thomas-Fermi equations similarly as in (44). In order to control the remainder terms, by Lemma 13 and Lemma 14, we have

$$\int \eta_r^2 \rho_0 \leq Cr^{-3}, \quad \int [\varphi_r^{\text{TF}}]_+^{\frac{5}{2}} = C \int (\rho_r^{\text{TF}}) \leq Cr^{-7}.$$

In order to bound the convolution term we use - as in the proof of Lemma 11 - the fact that  $|x|^{-1} - |x|^{-1} * g^2 \geq 0$ , and therefore also  $\rho_r^{\text{TF}} * (|x|^{-1} - |x|^{-1} * g^2) \geq 0$ . Since  $\varphi_r^{\text{TF}} = \chi_r^+ \Phi_r - \rho_r^{\text{TF}} * |x|^{-1}$ , we conclude that

$$\phi_r^{\text{TF}} - \phi_r^{\text{TF}} * g^2 \leq \chi_r^+ \Phi_r - (\chi_r^+ \Phi_r) * g^2.$$

Since  $\Phi_r$  is harmonic outside a ball of radius  $r$  and  $g$  is spherically symmetric,  $\chi_r^+ \Phi_r - (\chi_r^+ \Phi_r) * g^2$  is supported in  $\{r - s \leq |x| \leq r + s\}$  and, by Lemma 13, its absolute value is bounded by  $Cr^{-4}$ . Thus,

$$[\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+ \leq Cr^{-4} \mathbb{1}(r - s \leq |\cdot| \leq r + s)$$

and therefore,

$$\int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{\frac{5}{2}} \leq Cr^{-8} s.$$

To summarize, we have shown that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] - C(s^{-2} r^{-3} + r^{-37/5} s^{2/5}).$$

Optimising over  $s$  (leading to  $s \sim r^{11/6}$ ) we obtain (58).

**Conclusion** Combining (55) and (58) we infer that

$$D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] \leq Cr^{-7} (r^{\frac{1}{3}} + \lambda^{-2} r^2 + \lambda). \quad (59)$$

Now, we want to replace  $\eta_r^2$  by  $\chi_r^+$ . Using the Hardy-Littlewood-Sobolev inequality and (48), we get

$$\begin{aligned} D[\chi_r^+ \rho_0 - \eta_r^2 \rho_0] &\leq D[\mathbb{1}((1+\lambda)r \geq |x| \geq r) \rho_0] \\ &\leq C \|\mathbb{1}((1+\lambda)r \geq |x| \geq r) \rho_0\|_{L^{\frac{6}{5}}}^2 \\ &\leq C \left( \int \chi_r^+ \rho_0^{\frac{5}{3}} \right)^{\frac{6}{5}} \left( \int_{(1+\lambda)r \geq |x| \geq r} \right)^{\frac{7}{15}} \\ &\leq C(r^{-7})^{\frac{6}{5}} (\lambda r^3)^{\frac{7}{15}} = C \lambda^{\frac{7}{15}} r^{-7}. \end{aligned}$$

Therefore,

$$D[\chi_r^+ \rho_0 - \rho_r^{\text{TF}}] \leq 2D[\chi_r^+ \rho_0 - \eta_r^2 \rho_0] + 2D[\eta_r^2 \rho_0 - \rho_r^{\text{TF}}] \leq C r^{-7} \left( \lambda^{\frac{7}{15}} + r^{\frac{1}{3}} + \lambda^{-2} r^2 \right).$$

This bound is valid for all  $\lambda \in (0, 1/2]$  and by optimising over  $\lambda$  (leading to  $\lambda \sim r^{30/37}$ ) we obtain

$$D[\chi_r^+ \rho_0 - \rho_r^{\text{TF}}] \leq C r^{-7+1/3}.$$

□

**Step 5.** We are now in the position to prove Lemma 12.

*Proof of Lemma 12.* Let  $r \in [Z^{-\frac{1}{3}}, D]$  and  $|x| \geq r$ . As in [15, Eq. (97)], we can decompose

$$\begin{aligned} \Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x) &= \varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x) + \int_{|y| > |x|} \frac{\rho_r^{\text{TF}}(y) - \rho^{\text{TF}}(y)}{|x-y|} dy \\ &\quad + \int_{|y| < |x|} \frac{\rho_r^{\text{TF}}(y) - (\chi_r^+ \rho_0)(y)}{|x-y|} dy. \end{aligned}$$

By Lemma 15, we have

$$|\varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x)| \leq C \int_{|y| > |x|} \frac{(r/|y|)^\zeta |y|^{-6}}{|x-y|} dy \leq C(r/|x|)^\zeta |x|^{-4}.$$

Moreover, from (9), (48), (54) and Lemma 16, we get

$$\begin{aligned} \left| \int_{|y| < |x|} \frac{\rho_r^{\text{TF}}(y) - (\chi_r^+ \rho_0)(y)}{|x-y|} dy \right| &\leq C \|\rho_r^{\text{TF}} - \chi_r^+ \rho_0\|_{L^{5/3}}^{5/6} (|x| D[\rho_r^{\text{TF}} - \chi_r^+ \rho_0])^{\frac{1}{12}} \\ &\leq C(r^{-7})^{1/2} (|x| r^{-7+b})^{\frac{1}{12}} \\ &= C|x|^{-4+b/12} (|x|/r)^{4+1/12-b/12}. \end{aligned}$$

Thus, in summary, for all  $r \in [Z^{-1/3}, D]$  and  $|x| \geq r$ , we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C(r/|x|)^\zeta |x|^{-4} + C(|x|/r)^5 |x|^{-4+b/12}. \quad (60)$$

With (60) we will conclude now. First, we choose a  $\delta \in (0, 1)$  sufficiently small such that

$$\frac{1+\delta}{1-\delta} \left( \frac{49}{36} - a \right) < \frac{49}{36} \quad (61)$$

and

$$\frac{b}{12} - \frac{10\delta}{1-\delta} > 0. \quad (62)$$



Here,  $a$  and  $b$  are the constants from Lemma 11 and 16, respectively. Now, we have two cases.

**Case 1:**  $D^{1+\delta} \leq Z^{-\frac{1}{3}}$ . In this case, we simply use the initial step. Indeed, for all

$$|x| \leq D^{1-\delta} \leq (Z^{-\frac{1}{3}})^{\frac{1-\delta}{1+\delta}},$$

by Lemma 11 we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{49/36-a} |x|^{\frac{1}{12}} \leq C_1 |x|^{1/12-3\frac{1+\delta}{1-\delta}(49/36-a)}. \quad (63)$$

Note that

$$\frac{1}{12} - 3 \cdot \frac{49}{36} = -4.$$

Therefore, (61) implies that

$$\frac{1}{12} - \frac{3(1+\delta)}{1-\delta} \left( \frac{49}{36} - a \right) > -4.$$

**Case 2:**  $D^{1+\delta} \geq Z^{-\frac{1}{3}}$ . In this case, we use (60) with  $r = D^{1+\delta}$ . For all  $D \leq |x| \leq D^{1-\delta}$  we have

$$|x|^{2\delta/(1-\delta)} \leq \frac{r}{|x|} \leq |x|^\delta.$$

Hence, (60) implies that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\zeta\delta} + C|x|^{-4+b/12-10\delta/(1-\delta)}. \quad (64)$$

Both exponents of  $|x|$  are strictly greater than  $-4$  according to (62).

In summary, from (63) and (64), we conclude that in both cases,

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon}, \quad \forall D \leq |x| \leq D^{1-\delta}$$

with

$$\epsilon := \min \left\{ \frac{1}{12} - \frac{3(1+\delta)}{1-\delta} \left( \frac{49}{36} - a \right) + 4, \frac{b}{12} - \frac{10\delta}{1-\delta}, \zeta\delta \right\} > 0.$$

This finishes the proof of Lemma 12.  $\square$

## 9. PROOF OF THE MAIN THEOREMS

*Proof of Theorem 1.* Since we have already proved  $N \leq 2Z + C(Z^{\frac{2}{3}} + 1)$ , we are left with the case  $N \geq Z \geq 1$ . By Lemma 10, we find universal constants  $C, \epsilon, D > 0$  such that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon}, \quad \forall |x| \leq D. \quad (65)$$

In particular, (39) holds true with an universal constant  $\beta = CD^\epsilon$ . We can choose  $D$  small enough such that  $D \leq 1$  and  $\beta \leq 1$ , which allows us to apply Lemma 13. Then, using (45) and (47) with  $r = D$ , we find that

$$\int_{|x|>D} \rho_0 + \left| \int_{|x|<D} (\rho_0 - \rho^{\text{TF}}) \right| \leq C.$$

Since  $\int \rho^{\text{TF}} = Z$  we obtain the ionization bound

$$N = \int \rho_0 = \int_{|x|>D} \rho_0 + \int_{|x|<D} (\rho_0 - \rho^{\text{TF}}) + \int_{|x|<D} \rho^{\text{TF}} \leq C + Z.$$

□

*Proof of Theorem 2.* By Lemma 10, we find universal constants  $C, \epsilon, D > 0$  such that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon}, \quad \forall |x| \leq D.$$

As before, we can assume  $D \leq 1$  and  $CD^\epsilon \leq 1$  in order to apply Lemma 10.

Thus, we are left with the case  $|x| > D$ . For this we decompose

$$\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x) = \Phi_D(x) - \Phi_D^{\text{TF}} + \int_{|x| > |y| > D} \frac{\rho^{\text{TF}}(y) - \rho_0(y)}{|x-y|} dy. \quad (66)$$

Since  $\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)$  is harmonic for  $|x| > D$  and vanishes at infinity, we can apply Lemma 19 of [4] to find that

$$\sup_{|x| \geq D} |\Phi_D(x) - \Phi_D^{\text{TF}}(x)| = \sup_{|x|=D} |\Phi_D(x) - \Phi_D^{\text{TF}}(x)| \leq CD^{-4+\epsilon}.$$

Moreover, using the bound  $\rho^{\text{TF}}(y) \leq C|y|^{-6}$ , we can estimate

$$\int_{|x| > |y| > D} \frac{\rho_0(y)}{|x-y|} dy \leq C \int_{|x| > |y| > D} \frac{|y|^{-6}}{|x-y|} dy \leq CD^{-4}.$$

Finally, using (47) and (48), we have

$$\begin{aligned} \int_{|x| > |y| > D} \frac{\rho_0(y)}{|x-y|} &\leq \int_{|y| > D, |x-y| > D} \frac{\rho_0(y)}{|x-y|} + \int_{|y| > D \geq |x-y|} \frac{\rho_0(y)}{|x-y|} \\ &\leq \int_{|y| > D} \frac{\rho_0(y)}{D} + \left( \int_{|y| > D} \rho_0(y)^{5/3} dy \right)^{3/5} \left( \int_{D \geq |x-y|} \frac{1}{|x-y|^{5/2}} dy \right)^{2/5} \\ &\leq CD^{-4} + C(D^{-7})^{3/5} (\sqrt{D})^{2/5} \leq CD^{-4}. \end{aligned}$$

Thus, from (66) we conclude that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq CD^{-4}, \quad \forall |x| > D.$$

In summary,

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon} + CD^{-4}, \quad \forall |x| > 0$$

which concludes the proof. □

*Proof of Theorem 3.* As before, we start by using Lemma 10 to find universal constants  $C, \epsilon, D > 0$  such that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\epsilon}, \quad \forall |x| \leq D.$$

We assume that  $\epsilon \leq \zeta, D \leq 1$  and  $CD^\epsilon \leq 1$ . (Recall  $\zeta = (\sqrt{73} - 7)/2 \approx 0.77$ .) From (48) and the bound  $N \leq Z + C$  in Theorem 1, we get for all  $r \in (0, D]$ ,

$$\left| \int_{|y| \geq r} (\rho_0(y) - \rho^{\text{TF}}(y)) dy \right| = \left| N - Z - \int_{|y| < r} (\rho_0(y) - \rho^{\text{TF}}(y)) dy \right| \leq Cr^{-3+\epsilon}.$$

From [4, Theorem 11], we have

$$\left| \rho^{\text{TF}}(x) - \left( \frac{3A^{\text{TF}}}{5c^{\text{TF}}} \right)^{3/2} |x|^{-6} \right| \leq C|x|^{-6} \left( \frac{Z^{-1/3}}{|x|} \right)^\zeta, \quad \forall |x| \geq Z^{-1/3}$$

with  $A^{\text{TF}} = (5c^{\text{TF}})^3(3\pi^2)^{-1}$ . Inserting this in the latter estimate over  $|x| > r \geq Z^{-1/6}$  and using

$$\left(\frac{Z^{-1/3}}{|x|}\right)^\zeta \leq (r^2/r)^\zeta = r^\zeta \leq r^\epsilon$$

we obtain

$$\left| \int_{|x|>r} \rho^{\text{TF}}(x) dx - (B^{\text{TF}}/r)^3 \right| \leq Cr^{-3+\epsilon}, \quad \forall r \in [Z^{-1/6}, D],$$

where  $B^{\text{TF}} = 5c^{\text{TF}}(4/(3\pi^2))^{1/3}$ . Hence,

$$\left| \int_{|x|>r} \rho_0(x) dx - (B^{\text{TF}}/r)^3 \right| \leq Cr^{-3+\epsilon}, \quad \forall r \in [Z^{-1/6+\epsilon}]. \quad (67)$$

Applying (67) with  $r = D$  and  $r = Z^{-1/6}$  yields

$$\int_{|x|>D} \rho_0(x) dx \leq CD^{-3}, \quad \int_{|x|>Z^{-1/6}} \rho_0(x) dx \geq C^{-1}Z^{1/2}.$$

Thus, if we restrict to the case  $C^{-1}Z^{1/2} > \kappa > CD^{-3}$ ,  $R_\kappa := R(N, Z, \kappa) \in [Z^{1/6}, D]$  we can apply (67) with  $r = R_\kappa$ . We obtain

$$|\kappa - (B^{\text{TF}}/R_\kappa)^3| \leq CR_\kappa^{-3+\epsilon}.$$

Setting  $t := \kappa^{1/3}R_\kappa/B^{\text{TF}}$ , we can write this as

$$|t^3 - 1| \leq C(t\kappa^{-1/3})^\epsilon.$$

Using  $|t - 1| = \frac{|t^3 - 1|}{t^2 + t + 1} \leq \frac{|t^3 - 1|}{t^\epsilon}$  we conclude that

$$|\kappa^{1/3}R_\kappa/B^{\text{TF}} - 1| \leq C\kappa^{-\epsilon/3}.$$

Thus, if  $\kappa > CD^{-3}$ , then

$$\limsup_{N \geq Z \rightarrow \infty} |\kappa^{1/3}R_\kappa/B^{\text{TF}} - 1| \leq C\kappa^{-\epsilon/3},$$

which is equivalent to the desired estimate.  $\square$

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